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(21) International Application Number: PCT/US97/22464 (22) International Filing Date: 9 December 1997 (09.12.97) (30) Priority Data: 08/892,152 14 July 1997 (14.07.97) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (72) Inventor: FAROOQ, Omar, P.O. Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, Office of Intellectual Property Counsel, P.O. Box 33427, Saint Paul, MN 55133-3427 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: MICROPOROUS FLUORINATED SILICA AGGLOMERATE AND METHOD OF PREPARING AND USING SAME		
(57) Abstract Microporous fluorinated silica agglomerates are disclosed and their method of preparation from a reaction of colloidal silica of small particle sizes with an alkylamine (or a hindered amine) and hydrofluoric acid or with alkylammonium fluoride, under convenient laboratory conditions at an atmospheric pressure. The agglomerate is useful to interact with dispersants surrounding inkjet ink pigment particles.		

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**Microporous Fluorinated Silica Agglomerate
and Method of Preparing and Using Same**

5 Field of Invention

 This application relates to preparation of microporous fluorinated silica particles.

Background of Invention

10 Fluorinated silica supports containing organo-chromium compound or organomagnesium complexes were disclosed as a catalysts for the polymerization of ethylene and its copolymerization with other olefins in U.S. Pat. Nos. 4,100,337 and 4,359,403. The catalysts were prepared by mixing particles of reactive silica carrying superficial active -OH or oxide groups with a fluorine
15 compound e.g., ammonium fluoride, ammonium tetrafluoroborate or ammonium hexafluorosilicate and heating the mixture at 50°-700°C in presence of a solvent.

 Japanese Patent Publication J03279209-A disclosed a procedure of fluorination of white silica particle from tetraethylorthosilicate with hydrogen fluoride and heating the mixture to 600°C to obtain fluorinated black silica particle.

20 U.S. Pat. No. 5,064,796 disclosed an olefin polymerization catalyst produced by reacting a fluorinated silica support with a vanadium compound. The fluorinated silica is produced by mixing silica with a fluorine compound e.g., hydrogen fluoride, ammonium fluoride or a metal fluoride at 200-1000°C.

 U.S. Pat. No. 4,822,903 disclosed a fluorinated siliceous catalyst for
25 the catalytic synthesis of aromatic/aliphatic nitriles and is comprised of a plurality of silica particulates with the fluorine content ranging from about 0.1 to about 1% by weight based upon silica. The product gel was comminuted to grains which has a specific surface area ranging from about 200-250 m²/g, an average pore volume ranging from about 1-1.3 cm³/g and an average pore diameter ranging from about
30 100-150 Å. The fluorinated silica was characterized as a microporous acid silica at a pH 1-3 for use as a catalyst.

Summary of Invention

What is needed is a method of preparing microporous fluorinated silica agglomerate. The present invention solves that problem by utilizing a structuring agent for the preparation of microporous fluorinated silica agglomerate in a fluoride-ion medium. Whereas such procedure is known to have been used for the preparation of silica-rich zeolite (U.S. Pat. Nos. 3,702,886; 4,061,724; 4,073,865; and French Patent Publications 2,564,451 and 2,567,868), the present invention concerns the making of fluorinated silica in agglomerated form.

The present invention discloses the preparation of microporous fluorinated silica particles by reaction of colloidal silica of small particle sizes with an alkylamine (or a hindered amine) and hydrofluoric acid or with alkylammonium fluoride, under convenient laboratory conditions at an atmospheric pressure.

The materials in the dry form are microcrystalline or amorphous depending on the type of alkylamine used. The microporous characteristics of the silica agglomerate were established by scanning electron microscope (SEM), transmission electron micrography (TEM) and BET surface areas analyses.

The fluorinated silica agglomerate can be used as a pigment management system in the preparation of inkjet receptor media.

A feature of the fluorinated silica agglomerate is its functionalized character to permit interaction with dispersants that surround pigment particles of an inkjet ink.

An advantage of the fluorinated silica agglomerate is its ease of preparation under convenient and conventional laboratory and manufacturing conditions.

Further features and advantages emerge from a discussion of embodiments of the invention.

Embodiments of Invention

The use of fluoride ion as a flux component for the crystal growth from a melt is as well known as its mineralizing role in hydrothermal synthesis. But it is only recently that the role of fluoride ion was established in the

development of silica-rich microporous materials for the silica-rich zeolites discussed above. In this process the replacement of hydroxide anion by the fluoride ion as mineralizers make it possible to obtain silica-rich zeolite in acid pH.

In the present invention, the starting silica source is colloidal silica
5 (commercially available under the brand of "Nalco 2326" from Nalco Chemical Co.) of very small particle size (~2-5 nm) stabilized at pH ~12 wherein the mobilizing ions are the OH⁻ ions.

This silica sol can be diluted with water and mixed with varying amount of alkylamine at ambient temperature. Use of hydrofluoric acid to
10 fluorinate the silica can be arranged in a concentration of from about 40% to about 50% and preferably about 48% in water and prior to use, was further diluted to 20-24 % with deionized water.

Addition of the diluted hydrofluoric acid to the mechanically stirred mixture of silica and alkylamine at ambient temperature is likely to cause a mild
15 exothermicity which can be further cooled down by adding deionized water as required.

After the addition of all the hydrofluoric acid, the system can be stirred for half an hour to disperse the formed gel and then heated to vigorous water-reflux under mechanical stirring at about 100-200 rpm. The pH in the
20 system was ~4-6 in the beginning of the reaction and at this pH, F⁻ ions are the mobilizing agents from both hydrofluoric acid as well as from *in-situ*-generated alkylammonium fluoride.

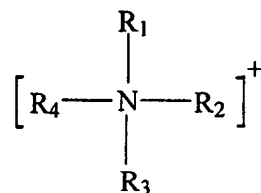
In an alternative embodiment, pre-prepared alkylammonium fluorides can be used as the mobilizing F⁻ ion source. At the end of the reaction,
25 the pH of the medium is about 7-8.

In the present invention, colloidal silica of very small particle size is used ranging from about 5 to about 10 nm and preferably from about 2 to about 5 nm. Numerous sources of silicon having a degree of oxidation of +4 can be used. Examples of suitable silica sources can include, but are not limited to those
30 selected from silica hydrogels, aerogels, xerogels, and colloidal suspensions

thereof; precipitated silica; alkylorthosilicates; hydrolyzable tetravalent silicon compound, (such as silicon halides) and the like.

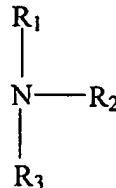
In order to make agglomeration of the silica particles, a structuring agent such as an alkylammonium cation was used. Fluorinated silica particles
 5 form agglomeration around the cation, wherein the cation acts as a templating cation. Structuring agents suitable for use according to the present invention are:

(a) quaternary alkylammonium Fluoride of formula I for the cation:



10 wherein R_1 to R_4 may be H or alkyl group or hybrid thereof representing primary, secondary, tertiary and quaternary alkylammonium cations.

(b) alkylamines of formula II:



15 wherein R_1 to R_4 may vary between H and alkyl groups representing primary, secondary and tertiary alkylamine. The R_1 - R_3 may altogether represent such alkyl groups as to form cyclic group(s) to give a hindered amine.

(c) any compound in Formula I or II in which nitrogen atom may
 20 be replaced by phosphorus atom.

Examples of suitable structuring agents consisting of alkylamines and the corresponding quaternary salts may include but are not limited to those selected from alkylamines such as methyl-, ethyl-, propyl- butyl-, amyl-,
 25 cycloalkyl-, alkylaryl-, aralkyl-, dialkyl-, trialkylamines. In the preferred

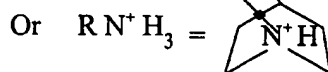
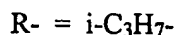
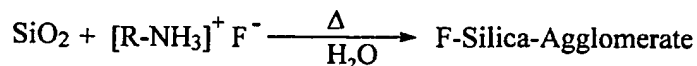
embodiment of the inventions, the structuring agents are the propylammonium cations including primary, secondary and tertiary propylammonium cations. More specifically the structuring agents are the isopropylammonium cations including isopropyl-, diisopropyl- and triisopropylammonium cations. And even more
5 specifically, isopropylammonium cation. The structuring agents may also a hindered amine e.g., a quinuclidine. The structuring agents may be introduced in the form of a base or a salt both being aqueous soluble, which determines the pH range of the reaction medium.

The preparation of fluorinated silica of the present invention may be
10 effected by heating the reaction mixture to a temperature of from approximately 60° to 200°C, preferably from 60° to 150°C over a period of time of approximately 1 to 5 days depending on the alkylamine used under a constant mechanical stirring at 100 to 200 rpm. The system is operated under one atmospheric pressure (no closed system e.g., autoclave, no autogenic pressure) under commonly used
15 laboratory conditions easily adaptable for industrial scale up, unlike those closed systems required for the preparation of siliceous zeolites in a fluoride ion-medium.

After stipulated time, there is obtained a dispersion of white opaque material in about 14-17% solid. The system may further be concentrated to obtain solid in the range of 18-23%. The dispersion thus obtained are suitable for use as
20 coatings after appropriate admixing with suitable binder(s) onto various substrates without further precipitation, isolation, separation or modification or treatment. The general procedure of preparation of the developed fluorinated silica agglomerate is outlined below in Formula III

25

Formula III



In the preparation of the fluorinated silica in the present invention, hydrofluoric acid or its alkylammonium salt was used as a dilute aqueous solution and when added to the mixture of silica source and/or alkylamine at ambient temperature, no observable corrosion was detected in the glassware or glass-stirrer which were repeatedly used. The hydrofluoric acid was therefore, found to be rapidly reacting with the amine in a reaction where it is used as such.

10 Examples

Example-1:

(a) SiO₂-i-pr-NH₂-HF system:

To 100g (15% solid, 15g, 0.245 mole) of a colloidal silica sol (Nalco 2326, average particle size ~ 4 nm) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer was added 45g (0.75 mole) isopropylamine under stirring at room temperature. To the mixture was dropwise added, at room temperature, after dilution with 100g de-ionized water, 30g (50% in water, 15g, 0.75 mole) hydrofluoric acid under stirring. The system was somewhat exothermic and during the addition of acid, 50g de-ionized water was added under stirring to disperse the formed gel. After the addition of all the acid, the system was heated to vigorous refluxing of water under mechanical stirring of about 150-200 rpm. After 3-5 days a white colloidal system resulted.

The material in combination with a binder copolymer of n-vinylpyrrolidone and dimethylaminoethylmethacrylate (copolymer-958, from ISP) was coated onto a polyvinyl chloride (PVC) base and dried at 100°C for 4 mins. The dry coating was subjected to SEM which showed a highly microporous surface. The sample had a surface porosity of 0.1-0.7µm.

The colloidal material in very dilute suspension was then subjected to TEM analysis which shows a microcrystalline morphology. Transmission electron micrograph of the sample, further, show that the material exists in cluster or agglomerate form - fluorinated silica agglomerate.

Part of the resulting sol was dried at 110°C to obtain a white powder which was analyzed for elements. The elemental analysis was as follows: %C 17.4, %H 5.1, %N 6.6, %Si 24.0, %F 26.0

X-ray diffraction pattern (Cu-Kα radiation, Philips vertical diffractometer) indicated that some of the developed materials are crystalline while some of them are amorphous. As carbon-chain length in the amine is decreased, crystallinity is decreased. Thus, amine of C₆-carbon gives more crystalline material than that of C₁-carbon. Material with cyclic amine e.g., with nuclidine gives completely amorphous material. The x-ray reflection peaks in any of the sample does not match with either mica or crystalline silica or pure-silica zeolite. The sharp x-ray diffraction pattern indicates ordered crystalline phase but the slopy and broad reflection at higher 2θ indicates some degree of disordered structures in the bulk.

Some of the fluorinated silica from isopropylammonium fluoride has been subjected to thermogravimetric analysis from ambient to 600°C in a platinum pan. About 14% weight loss was observed at about 225°C. The volatile components as identified by their mass spectra are found to be isopropylamine, isopropylammonium fluoride and water.

BET specific surface area measurement shows that the sample has a SSA of about 210-250m²/g with a pore volume of 0.12cc/g and a pore diameter of 110-140Å⁰.

(b) SiO₂-i-pr-NH₃⁺F system:

- 5 To 100g (15% solid, 15g, 0.245 mole) of a colloidal silica sol (Nalco 2326, average particle size ~ 4 nm) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer was added 59.3g (0.75 mole) isopropylammonium fluoride [prepared from 45g (0.75 mole) isopropylamine in 50g water and 30g (50% in water, 0.75 mole) hydrofluoric acid in 50g water at room temperature] under
10 stirring at room temperature. The system was somewhat exothermic and during the addition of the ammonium salt 100g de-ionized water was added under stirring to disperse the formed gel. The system was heated to vigorous refluxing of water under mechanical stirring of about 200 rpm. After 5-6 days a white colloidal system resulted.

15

Example-2:

SiO₂-(i-pr)₂-NH-HF system:

- To 100g (15% solid, 15g, 0.245 mole) of a colloidal silica sol (Nalco 2326, average particle size ~ 4 nm) in a three-neck flask fitted with a reflux condenser and a
20 mechanical stirrer was added 75.8g (0.75 mole) diisopropylamine under stirring at room temperature. To the mixture was dropwise added, at room temperature, 30g (50% in water, 15g, 0.75 mole) hydrogen fluoride under stirring. The system was somewhat exothermic and during the addition of acid 100g de-ionized water was added. After the addition of all the acid, the system was heated to vigorous
25 refluxing of water under mechanical stirring of about 200 rpm. After 3-5 days a white colloidal system resulted.

Example-3:

SiO₂-n-pr-NH₂-HF system:

- 30 To 100g (15% solid, 15g, 0.245 mole) of a colloidal silica sol (Nalco 2326, average particle size ~ 4 nm) in a three-neck flask fitted with a reflux condenser and a

mechanical stirrer was added 45g (0.75 mole) *n*-opropylamine under stirring at room temperature. To the mixture was dropwise added, at room temperature, 30g (50% in water, 15g, 0.75 mole) hydrogen fluoride under stirring. The system was somewhat exothermic and during the addition of acid 100g de-ionized water was added. After the addition of all the acid, the system was heated to vigorous refluxing of water under mechanical stirring of about 200 rpm. After 5-6 days a white colloidal system resulted.

Example-4:

The procedure in Example-3 was repeated replacing *n*-propylamine by *n*-butylamine and *n*-hexylamine to obtain the dispersion of aggregated silica particles.

Example-5:

To 40g (15% solid, 6g, 0.10 mole) of a colloidal silica sol (Nalco 2326, average particle size ~ 4 nm) in a three-neck flask fitted with a reflux condenser and a mechanical stirrer was added 10g (0.08 mole) quinuclidine under stirring at room temperature. To the mixture was dropwise added, at room temperature, after dilution with 110g de-ionized water, 8g (50% in water, 4g, 0.20 mole) hydrofluoric acid under stirring. After the addition of all the acid, the system was heated to vigorous refluxing of water under mechanical stirring of about 100-200 rpm for 18 hrs. After this period of time an opaque colloidal dispersion resulted.

The material in combination with a binder copolymer of *n*-vinylpyrrolidone and dimethylaminoethylmethacrylate (copolymer-958, from ISP) was coated onto a polyvinyl chloride (PVC) base and dried at 100°C for 4 mins. The dry coating was subjected to SEM analysis which showed a highly microporous surface. The sample had a surface porosity ranging from 0.1 to 1.2µm.

Preferred fluorinated silica agglomerates are those fluorinated silica wherein the silicon center is hexacoordinated.

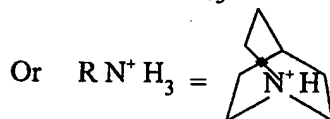
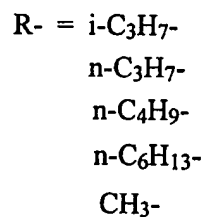
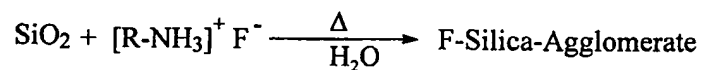
Fluorinated silica agglomerates can be used in any mechanism that requires both a microporous particulate regime and a functional surface for interaction with other compositions favorably with fluorinated surfaces of the particles of the agglomerates. One preferred usage is as a pigment management
5 system in association with a fluid management system in the formation of inkjet receptor media for pigment-based and dye-based inkjet inks.

The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A composition of matter, comprising:
fluorinated silica, SiO_2 , RNH_3^+F^- and H_2O wherein other materials
5 except the fluorinated silica are occluded in the bulk of material, wherein R is
selected from the group consisting of i- C_3H_7 ; n- C_3H_7 ; i- C_4H_9 ; i- C_3H_7 ; and CH_3 .
2. The composition of claim 1 prepared by digesting colloidal silica
of very small particle size with a source of fluoride ion under heating and
10 mechanical agitation and wherein the preparative conditions involve vigorous
water-reflux and mechanical agitation of about 100-200 revolutions per minute.
3. The composition of claims 1 or 2 wherein the F^- comprises
alkylammonium fluoride, which is derived from an alkylamine of C_6 - C_1 carbon and
15 HF.
4. The composition of any of claims 1-3 wherein the composition is
in the form of a colloidal dispersion in aqueous medium or in the form of a
fluorinated silica agglomerate impregnated with alkylamine, alkylammonium
20 fluoride, silica and water which are occluded in the bulk of the material and
wherein occluded labile compounds can be removed by thermal/vacuum means.
5. The composition of claim 4 wherein the fluorinated silica is in
the form of microcrystals with crystallite sizes in the range of 100-500Å⁰.
25
6. The composition of claim 4 wherein the fluorinated silica is in
agglomerated form and has a BET SSA in the range of 210-240 m²/g.
7. A method of making the fluorinated silica agglomerate of
30 composition of claim 1, comprising the steps of

(a) reacting colloidal silica with a fluorinated compound according to the following equation:



5

(b) forming a dispersion of the F-Silica Agglomerate.

8. The method of claim 7, wherein the reacting step comprises digesting colloidal silica of very small particle size with a source of fluoride ion under heating and mechanical agitation.

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9. The method of claim 7, wherein the reacting step comprises adding dilute hydrofluoric acid solution to a mixture of colloidal silica and an alkylamine at ambient temperature followed by aqueous refluxation.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 97/22464

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09C1/30

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C09C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 320 822 A (G.A. OZIN ET AL.) 14 June 1994 see column 6, line 33-50 see column 10, line 10-39; claims 1,4,12,16	1,3,4,7,8
A	US 4 054 689 A (D.W. CALVIN) 18 October 1977 see claim 1	1,7
A	EP 0 249 524 A (RHONE-POULENC CHIMIE) 16 December 1987 see claims 1,15,20	1,7

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 March 1998

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Information on patent family members

International Application No

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5320822 A	14-06-94	AT 143652 T DE 69214294 D DE 69214294 T EP 0613450 A JP 7503693 T WO 9310044 A	15-10-96 07-11-96 27-02-97 07-09-94 20-04-95 27-05-93
US 4054689 A	18-10-77	NONE	
EP 249524 A	16-12-87	FR 2599748 A FR 2614031 A BR 8703378 A CA 1300821 A CN 1027173 B DE 3776416 A JP 5022645 B JP 63040715 A JP 9175811 A MX 169545 B	11-12-87 21-10-88 15-03-88 19-05-92 28-12-94 12-03-92 30-03-93 22-02-88 08-07-97 12-07-93